Organic matter and fossil content in Serbian oil shales: Comparison with oil shales of Central Europe

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Abstract: Serbian Cenozoic lacustrine deposits contain the oil shales beside other sedimentary rock types. Organic matter of five randomly selected oil shale samples was characterized using elementary analysis and Rock-Eval pyrolysis. Fossil content and paleoecological conditions are characterized by palynological study. According to results of analyses, the samples from Subotinac, Vranye and Sushevlynska Bela Stena correspond to aquatic kerogen type I, being rich in organic carbon content (10–30 wt.%), as well as in hydrogen content expressed by hydrogen index (HI = 740–840 mg HC/g TOC). Sample from Mionica represents kerogen type III derived from woody material. According to maximal pyrolytic temperature all investigated samples are in early mature relict stage.

The oil shales originated in relatively large and deep lakes well supplied by nutritive elements and the water was eutrophic. The oil shales of Miocene age originated under subtropical climate conditions. The oil shale from Vranye Depression, Oligocene in age, originated in tropical to subtropical climate. The laminated structure of oil shales testifies the seasonal climatic changes. Small size of Botryococcus cells indicates the high reproduction potential of the algae.

The comparison with the Cenozoic oil shales of Central Europe indicates the differences in paleolake size, in paleoheat flow intensity and in carbonate lamina origin. Particularly the maar lakes of Slovakia and Hungary were small. The paleoheat flow in surroundings of Drienovec (Slovakia) was significantly lower in comparison with the Central Serbia and Kosovo. The Drienovec oil shales differ from those of Shushevlyanska Bela Stena in the origin of organic matter free lamina. Those of Drienovec originated by the activity of calcareous algae, those of Shushevlyanska Bela Stena are of chemogene origin.

Key words: paleolakes, Serbia, Cenozoic, oil shales, Botryococcaceae, pollen spectra, Rock–Eval pyrolysis, TOC

Introduction

In July 2003 one of us (Vass), being invited by Serbian Geological Society and personally by Nadezda Krstić, took part on the workshop Paleolimnology of the Serbian Neogene. During the field trip the samples of oil shales from four localities were collected. The sampled localities were (Fig. 1):

- Subotinac at town of Aleksinac, samples Srb-1 and 2
- Vranye Depression, sample Srb-3
- Mionica – bridge in the town, sample Srb-4
- Shushevlyanska Bela Stena, west of town Mionica, sample Srb-5

The lacustrine deposits are typical for the Serbian Neogene, including the oil shales. The paleolakes with oil shales by Obradović, Djurdjević-Colson & Vasić (1997) have been subdivided into two groups:

The oil shales of the first group are represented by an alternation of carbonate and kerogen (rich in organic matter) lamina. Such type of rock occurs in Valyevo–Mionica, Yadar (Jadar) and Pranyani depressions.

In the oil shales of second group the clay, marl or shale lamina alternate with lamina rich in kerogen. This type of oil shales occurs in Vranye and Aleksinac depressions.

The main purpose for sampling the Serbian oil shales was to get some information about shale's organic matter and fossil contents. The Serbian oil shales were compared with several oil shales of Central Europe, namely with Slovak localities – Pinciná (maar type), Drienovec (sea costal lagoon type, data from Vass et al., 1997; Milička & Vass, 2001), further with Hungarian localities Pula and Gérce (maar type, data from Bruckner-Wein & Hetényi, 1993) and Czech oil shale from Sokolov Coal Basin (data from Müller, 1987).

Method of study

The organic matter of oil shales was characterized using elementary analysis and Rock-Eval pyrolysis. Total organic and inorganic carbon (TOC, TIC) was determined in Czech Geological Survey Prague, branch Brno. Rock-Eval pyrolysis was carried out in Oil and

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Fig. 1. Sampled sites of oil shales in Serbia. Srb-1, 2 – Subotinac (Aleksinac Depression), Srb-3 - Goć – Denotin Deposit (Vranye Depression), Srb-4, 5 - Mionica, bridge in town and Shushevlyanska Bela Stena.

Gas Institute Kraków and interpreted in the sense of Espitalié et al. (1986).

For palynological study the fine-grained sediment samples, about 20 g in volume, were treated using a standard palynological extraction technique involving HCl – HF – HCl and heavy liquid treatment (solution of cadmium iodide, potassium iodide of a specific gravity of 2.0), next the obtained organic matter was macerated in 30 % hydrogen peroxide solution, in KOH and subjected to acetolysis by Erdtman's (1943, 1960) method.

One to three microscopic preparations were made from each sample according to the amount of the palynomorphs. Samples were sieved on 10 μm sieves.

General characteristics of sampled depressions

Samples were taken from two very different geotectonic units. First group of samples is from Lower Miocene conformably topping Paleogene turbidite deposits of the Vardar Zone, this time the strait between Dinaric and Carpatho-Balkan islands. Others were taken from the deposits of Middle Miocene Serbian Lake situated in the middle of Balkan Land formed by uniting of mentioned islands.

The Vardar Zone was an area of deep sea deposition for very long time (since Carboniferous). The last phase with turbiditic sedimentation took place continuously from the Upper Cretaceous through Upper Oligocene what is corroborated by calcareous nannoplankton and dinoflagellate cysts (Capoa & Radoičić, 2002). Aside off the straight some lagoons were formed, like acidic Shumadia Lake (Krstic et al., 2003), being also dwelled by marine fishes (mugilid) except for the period of sprawling when they migrated to the sea water (Gaudant, 2002) of nearby straight. The closing of the straight had not stopped the sedimentation in these lagoons, but changed them into lakes, like lakes of Aleksinac and Polyanica (Goc-Devotin), deep enough to house meromictic lakes, their profundal filled by oil shales.

The Serbian Lake (Krstić, 1996) was formed along the postcollisional spreading area, further modified by bending of Carpathian-Balkan arc. Close to Belgrade conformably on the Serbian Lake sediments the Middle Badenian sequences lie. The lake, spotted by some islands, in its deeper subdepressions had the water stratification, thus the conditions convenient for the oil shale origin.

The most oil bearing is the Valjevo-Mionica Depression more than 20 km long and 10 km wide. Four depth zones were distinguished (Jovanovic *et al.*, 2005):

- Lentic environment, in places with sedge, but mostly with fossiliferous Tolić Limestone around Paštrić, Tolić and other villages was in the past the area of floating plants producing lacustrine chalk
- In the southeastern and northern parts of depression the moderately deep and well aerated portion of lake, with marly silt sedimentation, contains ostracodes *Ohridiella sabantae, Cypria* and, in rare places, *Congeria, Micromelania* (Jovanović et al., 2005) as some other molluscs from genera *Pisidium, Planorbis, Prosothenia, Nematurella (?), Lymnea, Theodoxus* (Dolić, 1983)
- Third is the belt where ostracode laminite indicates the ancient position of mesolimnion - there alternate ostracode-bearing lamina brought by seepage of warmer and more dense water from epilimnion with lamina deriving from hypolimnion pulsations – exactly the sample Srb-4 was taken there.
- To the fourth, the lake profundal winnow redundancy of *Botryococcus* algae when water was calm, while when water was agitated by the turbidites, the silt was settled - both together making lamina. Today the main oil shale body is 8 x 2.5 km large (Pantić et al., 1980) and covers the central and southern parts of the Valjevo-Mionica depression. It crops out again northward on the other side of Kolubrara fault.

Sampled places are app. 7.5 km apart and belong to two depth zones: the mesolimnion (Mionica) and hypolimnion Shushevlyanska Bela Stena.

Aleksinac Depression

An exhausting geological description of the Aleksinac Depression was given by Stevanović (1964) including the story of the coal bearing depression investigation from the end of 18. century (list of papers see in Stevanović references).

The depression filled by Cenozoic deposits is surrounded and underlain, sometimes overthrusted, by the Lower Paleozoic metamorphic rocks (Krstić, B. et al., 1980) possibly Ordovician – Silurian in age (Kreutner & Krstic, B., 2003). The depression sedimentary fill containing the coal seams and oil shales, being Oligocene-Lower Miocene (Petković & Ćićulić, 1962) or Lower Miocene (Stevanović, 1964) in age is of lacustrine origin. According to Krstić, B. et al. (1980) these sediments are thick up to 900–1000 m. The profundal lake deposits are represented by oil shales. The marginal, or coastal facies are represented by paludal – lacustrine deposits including the coal seams. The depression fill is subdivided into three units (informal formations, Obradovič et al., 1997):

- Lower formation with three oil shale horizons of the total thickness 520 m,
- Middle formation contains the coal seam thick 2–4 m, exceptionally 15 m and oil shale thick up to 60–100 m.
- Upper formation consists of marlstone, its thickness is up to 200 m.

The basal deposits of the depression fill: conglomerate and sandstone with thin layers of conglomerate of alluvial origin transgressively lie on the crystalline basement. Above the fine-grained sandstone, the claystone, marl and oil shale occur. The coal of middle formation manifests the paludal–lacustrine or marsh–swamp origin. Directly over the coal the oil shale thick up to 100 m lies (representing marginal facies?). The upper member is built up by marlstone with 3–5 % of organic matter (kerogen) grading upward in white marlstone with thin intercalations of the marly clay and tuff.

The oil shales are laminated. The lamina rich in organic matter alternate with lamina of marl and/or clay, rarely of dolomicrite. The kerogen is of type I, less of type II (Obradovič et al., 1997). The huminite reflectance varies from 0.25 to 1.5 % R_o. The TOC contents range between 12 wt.% and 24 wt.%.

Valyevo–Mionica Depression

The depression elongated in direction W–E is surrounded on the north by the Paleozoic and Lower Triassic clastic rocks and on the south by Middle Triassic limestone. Simplified lithological column is in Fig. 2. The thickness of the depression fill is ca. 250 m. According to Andjelković (1989) the depression fill is Lower Miocene in age. According to new stratigraphy revision by Jovanović et al. (2005) the age of depression fill is Middle Miocene – Pliocene and the oil shale sequence occupying approximately middle part of the column is considered to be Upper Miocene in age. The lower and marginal parts of the depression fill are built up by limestone, marlstone, sandy marlstone and clay marlstone with sandstone intercalations. The profundal (intrabasinal) sediments consist of the marlstone, oil shale, tuff with thin layers or bodies of searlesite ($NaBSi_2O_5(OH)_2$) and analcime. The thickness of the whole sequence is larger at Shushevlyanska Bela Stena, towards north the sequence is divided into two parts and is thinner. The uppermost part of depression fill deposited in shallow water and the dominant lithotype is limestone with chert. The oil shale is laminated, the lamina rich in organic matter alternate

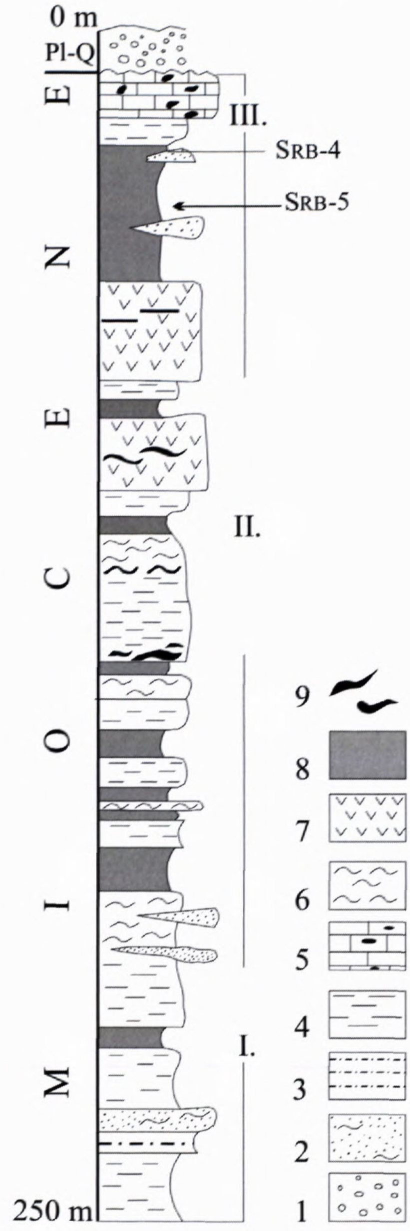

Fig. 2. Schematic lithological column of Valyevo–Mionica Depression fill. 1 – conglomerate, 2 – sandstone and marly sandstone, 3 – siltstone, 4 – claystone, 5 – limestone with chert concretions, 6 - marlstone, dolomitic marlstone, 7 – tuff, 8 – oil shale, 9 – searlesite and analcime bodies. I – marginal facies, II – intrabasinal facies, III – shallow water facies with chert concretions. (After Obradović, Djurdjević-Colson & Vasić, 1997).

with lamina of dolomicrite, rarely calcite. In the dolomicrite lamina the authigenic minerals searlesite and analcime appear. The lamination is often deformed by the authigenic minerals grow. The authigenic minerals mentioned, especially the trona, shortite and even gypsum occurring in same samples, indicating the salinity rise in the paleolake and interstitial brine. The ammoniacal nitrogen is present as a result of the organic matter decay (Obradovič et. al., 1997).

The kerogen of the Valyevo–Mionica depression belongs to the type I and II (Obradovič et al., 1997). The huminite reflectance R_o is 0.26 % (Ercegovac, 1990). Algae of *Botryococcus* type are well preserved.

Polyanica Depression north of Vranye

The Vranye Depression situated in Southern Serbia is surrounded and underlain by the Riphean–Cambrian crystalline schists of the Serbian–Macedonian Massif: gneiss, leptynolite, micaschist, amphibolite schists and quartzite. The deep borehole penetrates these rock types in the central part of depression in depth around 1500 to 2000 m (Krizak, 2003). The depression is divided into a smaller and older (Oligocene) Polyanica partial depression and a larger and younger (Middle Miocene) Vranye s. s. partial depression. The depression opened during the Paleogene and was filled by Paleocene–Eocene (its southernmost Pćinya part) and Oligocene deposits (Mihajlović, 1985) as well as by the Miocene and Pliocene deposits (Vukanović et al., 1977). The sedimentation was accompanied by volcanic activity culminating in the Middle Miocene.

The basin fill was subdivided by Jovanović and Novković (1988) into three formations or complexes:

Pćinya Formation: tuffaceous deposits, tuff, turbidites of total thickness of 400 m, Paleocene – Eocene in age, having the marine deep gulf origin. Far to the south the marine molluscs were found (at Ovće Polye, Macedonia).

Buśtranye – Polyanica Formation with the oil shales thick up to 1100 m, Oligocene in age, the formation is of lagoonal origin (marine Lower Oligocene corals were found westwards close to the town Gnyilane).

Vranye Complex containing several formations having the lithological contents: tuff, zeolite, bentonite, diatomite, oil shale and lignite. The age of the complex main part is Middle Miocene and the total thickness is 2 000 m or more. The complex is of volcanic and lacustrine origin.

The Oligocene lagoonal Polyanica Formation deposits lying unconformably on the Pćinya marine gulf/strait formation begin with the fluvial conglomerate, coarse sandstone and limestone originated on the river mudflats. The asphalt also occurs there. The lacustrine profundal and/or intradepressional deposits are marlstone, tuff, tuffaceous rocks and oil shales. The age was determined on the base of macroflora by Mihajlović (1985). The oil shales are developed in four horizons, their thickness varies from 4 to 15 m. The uppermost Oligocene consists of marlstone, shale, claystone and carbonates.

The Miocene Complex is composed by fluvial and marginal lacustrine deposits as conglomerate, gravel and sandstone. The intradepressional or profundal deposits are composed of oil shales covered with lapilli tuff and tuffaceous deposits. The uppermost rocks of the Miocene complex are marlstone, claystone, tuff being often transformed in zeolite (Obradović & Vlasić, 1990), tuffaceous rocks, while diatomite and lignite may be Pliocene in age (Vukanović et al., 1977).

The Oligocene oil shales are laminated rocks. The lamina rich in organic matter alternate with the lamina of clay. The kerogen is mostly of type I, partly type II. Type III is randomly present, too. The reflectance of bituminite is 0.10–0.30 % R_o and of huminite is 0.35–0.45 % R_o (Ercegovac, 1990).

Results of collected samples study

Samples of Serbian oil shales collected in 2003 belong to both types defined by Obradović et al. (1997). The samples taken in town of Mionica and at the site Shushevlyanska Bela Stena are of the first group. The samples coming from village of Subotinac near town of Aleksinac and from Vranye Depression belong to the second group.

Characteristics of oil shale samples from Subotinac–Aleksinac Depression

The samples (Srb-1 and 2) have been collected in the abandoned pit near the village of Subotinac, where the main oil shale horizon in the hanging wall of the coal bearing horizon outcrops (Fig. 3). The sampled oil shale consists of alternating grey marl and dark lamina rich in organic matter.

The estimated TOC contents are of 25.9 and 28.6 wt.%. According to the Rock-Eval pyrolysis the free hydrocarbon (S1) contents are of 2.87 and 3.33 mg and fixed hydrocarbon (S2) contents are of 213.4 and 216.1 mg. The hydrogen index (HI) ranges from 747 to 835 g of TOC and the maximum pyrolysis temperature T max reaches 440 and 446 °C (Tab. 1).

The clay minerals were studied by X-ray diffraction method. The samples from all studied localities are characteristic by low reflexion intensity resulting from the low clay mineral contents and probably the low structural organization of clay minerals along with the increased background, signalizing the presence of amorphous organic matter. The clay minerals of the oil shale from Subotinac (sample Srb-2a) are illite, smectite, eventually I-S mineral of high expandability and possibly the clinoptilolite (one reflex only). The rock exchange capacity is of 232 and 238. The specific surface is of 359.41 and 347.32 $m^2 . g^{-1}$ (Uhlík, written com.).

The most common fossils in the oil shale are algae occurring in colonies. The channel like structures on the colonies margins resemble the colonies of the Botryococcaceae family with strongly reduced magnitude of the channels. The pollen spectrum is uniform, not diversified represented by gathered unidentified amorphous not coalfield organic matter and by few algae. The pollen grains of *Pinus, Cathaya* and *Quercus* type *ilex* are the very rare admixture in the pollen spectrum. They indicate a subtropical climate.

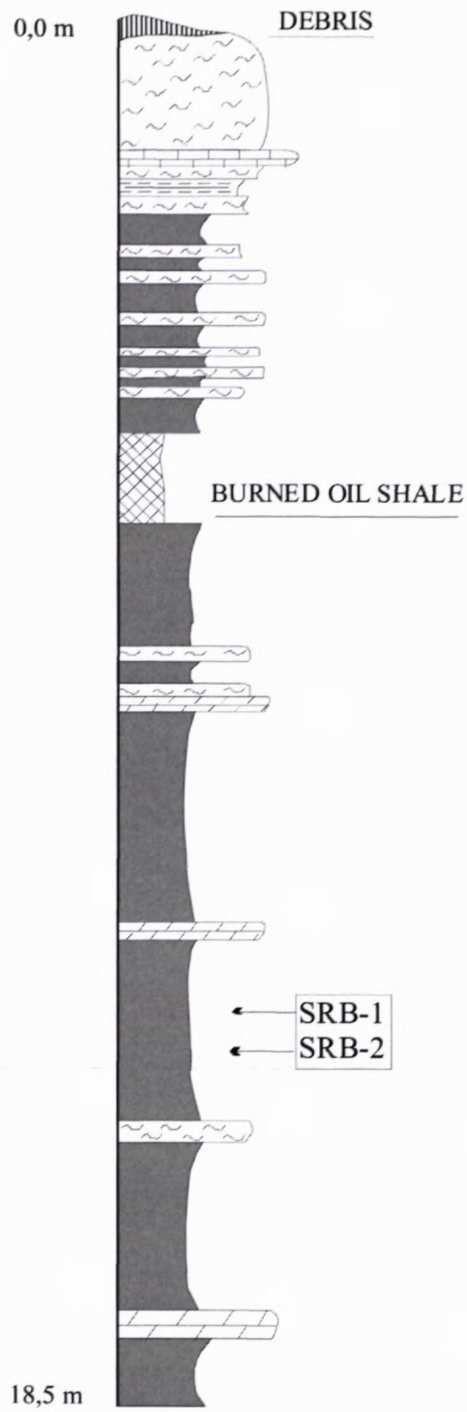

Fig. 3. Lithological column of abandoned oil shale pit (a slope above the rivulet Moravica), Subotinac village at Aleksinac (Kaśanin – Grubin, 1996). For explanations see Fig. 2.

Characteristics of samples from Mionica – bridge and Shushevlyanska Bela Stena

In the valley of **Ribnica river** 2 km downstream of the town Mionica the oil shale bearing horizon outcrops. The outcropping rocks represent three different lake environments (Jovanović et al. 2005). At the village Pashtrić the shallow lacustrine deposits – massive and laminated carbonates (chalk) outcrop. The massive carbonate contains the molluscs Congeria sp., Planorbis sp. and Micromelania sp. as well as the ostracodes – Candoninae. At the bridge in Mionica town the thermocline belt occurs. Several kilometres downstream of the river the profundal laminites – oil shales outcrop. The light grey to white dolomicrite lamina alternate with dark lamina rich in algal organic matter. The flora indicates the Middle Miocene age (Pantić et al., 1980).

In the **Mionica town** near bridge on the Ribnica river thin bedded or laminated siltstone outcrops. The bedding planes are covered by valves of ostracodes. The horizon originated when the dense mineralized water from the lake water level submitted to evaporation seeps down the sublittoral bottom, struck the thermocline and the speed of seepage decelerated. The ostracodes sailing in the mineralized water fell down and recently occur on the siltstone bedding planes (Jovanović et al., 2005).

The sample taken from the rock (Srb-4) is relatively poor in organic matter. TOC content is of 1.11 wt.%. The content of free hydrocarbons (S1) is of 0.18 mg, the fixed hydrocarbon amount is 2.9 mg. The hydrogen index is 259 mg HC in g of TOC. The maximum pyrolysis temperature (Tmax) is of 439 °C (Tab. 1).

The clay minerals are represented by illite and smectite or by I-S mineral of a high expandability. The X-ray analyses indicate the low contents of chlorite, kaolinite and quartz. The rock exchange capacity is 118 and 131. The specific surface is 174.92 and 191.99 $m^2.g^{-1}$ (Uhlík, written com.)

The pollen spectrum is rich and extremely diversified. The warm - temperate arctotertiary elements are dominant and the paleotropical taxa are sub dominant. The thermophile elements are represented by Sapotaceae, *Engelhardia, Platycarya, Castanea, Ilex, Distylium, Symplocos and Myrica.* The humid plants are represented by *Alnus, Ulmus, Salix, Nyssa and Osmunda.* The mesophytic taxa are represented by *Quercus, Fagus, Pterocarya, Carya, Zelkova, Carpinus and Juglans.* The mountain vegetation is represented by *Picea, Abies, Cedrus and Sciadopytis. Pinaceae* family is represented by *Pinus and Cathaya. Graminae* are present, too. The algae occur sporadically. According to the presence of evergreens *Engelhardia, Platycarya, Castanopsis, Sapotaceae,* the climate was subtropical.

Near the town of Valyevo the **Shushevlyanska Bela Stena** rocks are outcropping. The oil shale is laminated, the lamina rich in organic matter alternate with lamina of dolomicrite. The rock (Srb-5) is relatively rich in organic matter. TOC content is of 15.85 wt.% and the inorganic C content is of 2.47 wt.%. The content of free hydrocarbons is 3.76 mg fixed hydrocarbon amount is of 128.4 mg. The estimated hydrogen index (HI = 810) is considerably high. Tmax is of 439 °C (Tab. 1).

The clay minerals are represented by illite and kaolinite or chlorite of low concentration. Beside it the quartz, albite and K-feldspar are present. The rock exchange capacity is 132 and 142. The specific surface is 199.70 and 208.44 m^2. g^{-1}(Uhlík, written com.)

The palynospectrum is diversified. Beside the amorphous organic matter there are *Myrica, Engelhardia, Alnus, Nyssa, Pinus, Cathaya and Tsuga.* The climate was subtropical and humid.

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Tab. 1 Organic-geochemical characteristic of Serbian oil-shales

Locality	Sample code	Stratigraphy	Depth m	TIC	TOC wt.%	S1 mgHC/g r.	S2 mgCO/g r.	HI mgCO/g TOC	OI $mgCO_2$/ TOC	PI	GP	T_{max} °C	Kerogen type
Subonatic (a)	SRB1	Lower Miocene	surface	0.52	28.60	2.87	213.4	747	32	0.01	216.31	440	I
Subonatic (a)	SRB2	Lower Miocene	surface	0.05	25.89	3.33	216.1	835	35	0.02	219.39	446	I
Vranye	SRB3	Middle Miocene	surface	0.05	9.63	0.95	71.3	741	30	0.01	72.27	438	I
Mionica*	SRB4	Middle Miocene	surface	2.30	1.11	0.18	2.9	259	50	0.06	3.06	439	III
Shushevlyan-ska Bela Stena	SRB5	Middle Miocene	surface	2.50	15.85	3.76	128.4	810	34	0.03	132.15	439	I

TOC, S1, S2, HI, OI, PI, GPm, T_{max} – Rock-Eval pyrolysis parameters: TOC – total organic carbon; S1 – free hydrocarbons; S2 – fixed hydrocarbons-residual hydrocarbon potential; HI – hydrogen index; OI – oxygen index; PI – production index; GP – genetic potential; Mionica: claystone with low organic matter content not representing an oil shale.*

Tab. 2 Comparison of selected organic-geochemical characteristics of Serbian oil-shales with other localities in Central Europe

Locality	Well	Depth m	TOC		S1		S2		HI		T_{max}		Number of samples
			extent	x	extent	x	extent	x	extent	x	extent	x	
Serbian oil shales Lower – Middle Miocene	outcrops	surface	9.63-28.6	19.99	0.95-3.76	2.72	71.30-216.10	157.29	741-835	783	438-466	440	4
Slovakia (Drienovec) Eocene – Oligocene	VD 2	577-622	1.23-5.6	3.49	0.10-0.38	0.20	7.02-32.56	21.19	571-667	606	418-434	426	5
Slovakia (Pinciná) Pontian	VPA 1, 3, 4, 5, 7	7.0-48.0	3.81-28.58	8.90	0.29-14.36	3.80	10.5-169.00	41.50	279-962	451	426-442	438	91
Hungary (Pula) Upper Pannonian – Pliocene	Put 30	6.3-50.5	2.50-31.00	15.30	0.29-13.74	6.10	7.49-265.54	100.83	293-769	569	438-444	440	93
Hungary (Gércse) Upper Pannonian – Pliocene	Gét 6	16.3-65.0	2.39-9.84	5.92	2.04-15.46	8.05	8.91-73.63	34.68	372-1007	566	391-433	422	23
Czech Republic (Sokolov Basin) Cypris Beds (Middle Miocene)	open coal-mine	subsurface		6.47		0.02		60.9		939		439	77

TOC, S1, S2, HI, Tmax – Rock-Eval pyrolysis parameters as in table 1: x – average value

Characteristic of samples from Polyanica Depression (north of Vranye)

The main occurrence of oil shales in **Vranye** surroundings belongs to Oligocene (Buśtranye – Polyanica Formation). The oil shales form four seams. The maximum thickness of the uppermost one (seam I) is 15 m and the quality concerning the crude oil content is the best – in average of 4.4 % (Novković et al., 1986).

From the Goć–Devotin oil shale deposit, borehole Dj-3, depth 3.0–8.0 m, the following pollen spectrum was described: *Laevigatoporitess haardti, Polypodiaceoisporites marxheimensis, Punctatisporites crassiexinus, Foraminisporites granoverrucatus, Monocolpopollenites tranquilus – Palmae, Monocolpopollenites tranquilus tranquilus – Palmae, Inaperturopollenites hiatus – Taxodium, Pityosporites microalatus – Pinus haplpxilon, Pityosporites labdctus – Pinus silvestris, Piceapolis planoides – Picea, Cedripites crassiunulicristatus – Cedrus Podocarpidites sp., Polyvestibulopollenites verus var. multiporatus – Alnus, Polyvestibulopollenites verus – Alnus, Tricolporopollenites dolium – Rhus, Tricolporopollenites pseudocingulum – Rhus, Tricolporopollenites megaexactus bruehlensis – Cyrillacea, Tricolporopollenites krushi pseudolaesus – Nyssacea, Ephedrites sp., Tricolpopollenites henrici – Quercus, Tetracolpopollenites macroechinatus – Sapotaceae, Tetracolpopollenites sapotoides – Sapotaceae, Tetracolpopollenites obscurus – Sapotaceae, Tetracolpopollenites sp., Tetradopollenites callidus – Ericaceae, Polyadopollenites multipartitus – Mimosaceae, Cercidiphylum sp.* (L. Dimić unpublished data). The assemblage indicates tropical to subtropical climate.

The sample (Srb 3) was taken from uppermost seam of the Goć-Devotin oil shale deposit (Fig. 4). The Rock-Eval pyrolysis yields the following data: TOC content 9.63 wt.%, free hydrocarbon content 0.95 mg, fixed hydrocarbon content 71.30 mg. The hydrogene index reaches to 741 and Tmax to 438 °C (Tab. 1).

The rock exchange capacity is 96 and 102. The specific surface is 140.97 and 145.18 $m^2.g^{-1}$ (Uhlík, written com.)

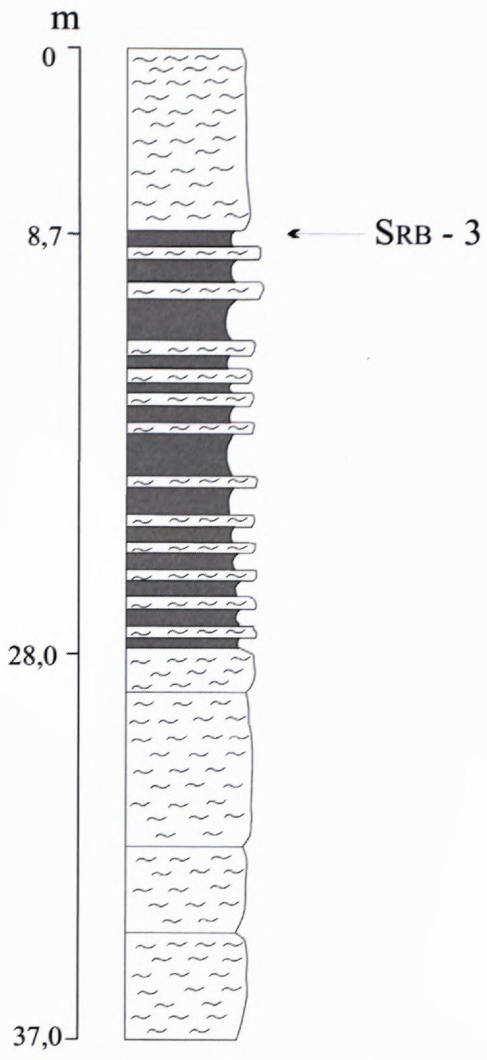

Fig. 4. Borehole D-3/82 lithologic profile, Goć – Devotin deposit, north of Polyanica, Vranye Depression. (After Novković et al., 1986). For explanation see Fig. 2.

Discussion

The oil shale of Subotinac under the study similarly as the Cainozoic Middle European laminated oil shales (Fig. 13) originated in relatively deep lakes (about 40 m or deeper). In such lakes in humid and moderate warm or subtropic climate during the summer the water mass was stratified and the lake underwent a period of stagnation. The upper water layer – epilimnion – heated by solar radiation was relatively hot and well supplied by mineral nutrients swash down into lake from the weathered rocks of lake source area. The nutrients came particularly from the volcanic rocks of the intermediate or basic chemical composition rich in K, Ca, Mg and P. Such rocks, as from the geologic background of the lakes follows, have been present in the lakes surroundings. The lake water table was calm and quiet. In such conditions the water of epilimnion became quickly eutrophic and overpopulated by microflora, particularly by the Botryococcaceae. The dead clusters of *Botryococcus* fell down on the bottom and in anaerobic conditions of the hypolimnion, buried by fine clastics the organic matter has been fossilized. By this way the dark lamina rich in organic matter of the oil shale originated. With approaching of the late autumn and winter the water stratification collapsed. The period of lake stagnation was replaced by period of water circulation. The life conditions, as well as conditions of the organic matter fossilization at the lake bottom become worse and in such conditions the lamina poor in organic matter originated.

The oil shale of Vranye Depression, Oligocene in age, originated in tropical climate that is proved by the sporomorphs assemblage. The tropical lakes have different seasonal cycles in comparison with the temperate (and subtropic) ones. In recent meromictic Lake Malawi in Africa, laminated deposits originate. The lamination reflects the seasonal change: dry windy season (April – October) with high bioproductivity in the lake and wet, but calm season with low bioproductivity (Pilskaln & Johnson, 1991; fide Cohen, 2003).

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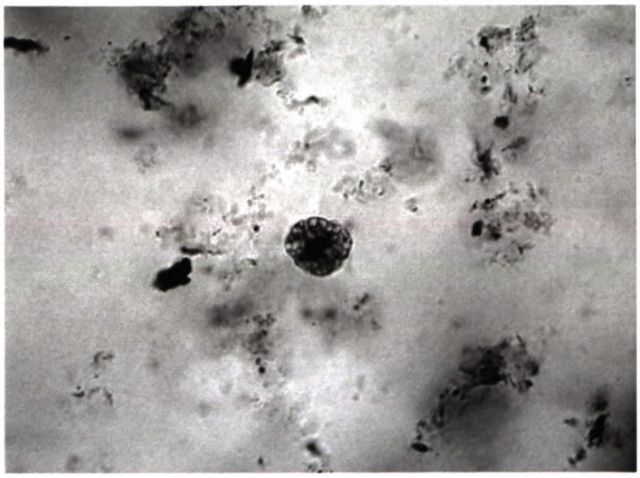

Fig. 5

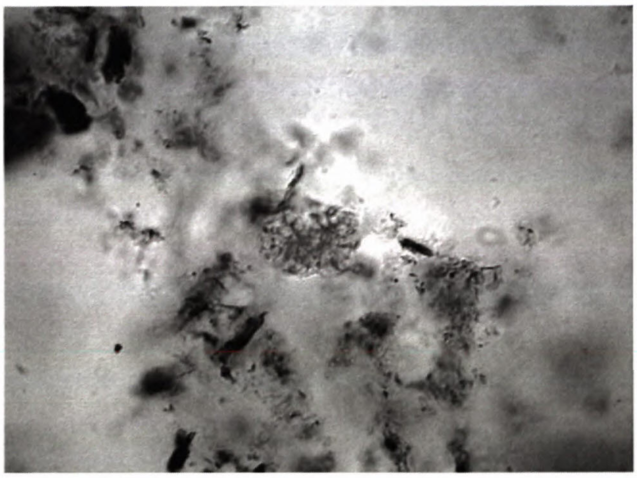

Fig. 6

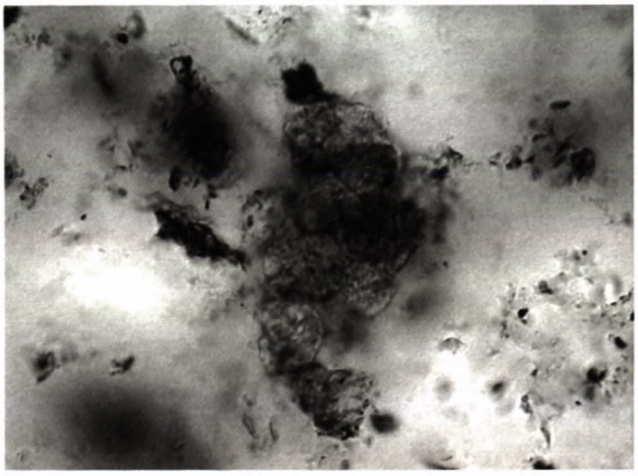

Fig. 7

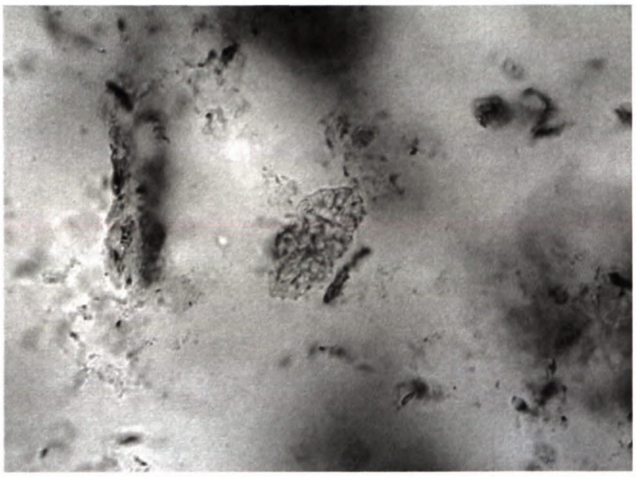

Fig. 8

Figs. 5–8. Clusters of Botryococcus braunii Kützing 1849, magn. 630x, Aleksinac. Individual forms are small as a result of excellent life conditions and of high reproduction potential.

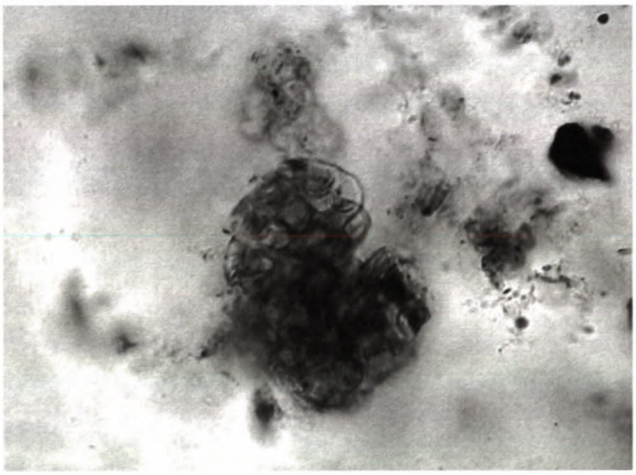

Fig. 9. Botryococcus braunii Kützing 1849, magn. 630x, Pinciná, Slovakia. In comparison with the forms of Aleksinac, the forms of Pinciná are larger testifying slower growth in the slightly worse life conditions.

According to Rock-Eval pyrolysis of the samples from Subotinac, Vranje and Shushevlyanska Bela Stena (Srb1, 2, 3 and 5 in Table 1) the kerogen of the sampled oil shales represents the aquatic kerogen type I (Fig. 11). The kerogen of the Middle Europe Cenozoic oil shales (alginite) originated in basalt maar lakes represents a mixed type I-II (the aquatic and aquatic/terrestrial). The reason of different kerogen type in compared paleolakes may be the different lake extent. The paleolakes of Aleksinac, Vranye and Mionica (Shushevlyanska Bela Stena) have been of larger extent. Particularly the maar lakes where the alginite originated have been small. For example the maar lake at Pinciná (Southern Slovakia) has been only 0.25 km^2 large (Vass et al., 1997). In small lakes during the summer stagnation beside dominant Algae larger water plants vegetated being the source of kerogen type II in the organic matter of bottom sediment. The large lakes epilimnion especially at some distance of the coast was free of larger water plants and the Algae have had excellent life conditions producing the kerogen type I in the bottom sediment. This idea is supported by high contents of organic matter in the oil shales generated in large lakes (see Tab.1 and compare with Tab. 2) as well as the *Botryococcus* cells form testify the very good condition for Algae quick bloom. In the oil shales particularly from Aleksinac Depression exclusively small types of *Botryococcus braunii* Kützing have been found

(Figs. 5–8). Small forms of Botryococcaceae are typical for the biologically active water environment, when this algae have high reproduction potential. The large size of *Botryococcus brauni* cells from Pinciná testifies the slower grow of the algae (Fig. 9).

Obradović and Vlasič (2008), examined a set of oil shales from Aleksinac Depression using gas chromatography. According to these results the pristane/phytane ratio is generally less than 1, indicating an origin in a saline lake rich in dissolved carbonates (Rohrback, 1983). The n-alkanes range from n-C_{16} to n-C_{33}; n-C_{27} is generally the most abundant n-alkane.

The oil shale generation in large paleolakes is usually in genetic relation with the coal seams generation. The lakes before got deeper and perhaps larger they have been shallow swamps or bogs convenient for the coal generation. It is valid particularly for paleolake of Aleksinac Depression, the Sokolov Coal Basin in Bohemia and the oil shale from Šiatorská Bukovinka (Southern Slovakia) associated with the coal bearing Pôtor Member of Salgótarján Formation (Vass, 2001). The kerogen of oil shale from the Somodi Formation at Drienovec (SE Slovakia) being in genetic relation with glance brown coal (Vass et al. 1994) is at boundary between type I and II (Milička & Vass, 2001).

The inorganic carbon contents in the oil shale of Shushevlyanska Bela Stena (Srb. 5) is relatively high. The high contents of inorganic carbon also in oil shale from Drienovec (but almost 5 tens higher as in Srb. 5 sample, Fig. l) was measured. In both rocks the dark in organic matter rich lamina alternate with white carbonatic lamina. The carbonatic lamina in Drienovec oil shale are of organic origin being build up by "carpets" of calcareous Algae (thin stromatolites; Mello in Vass et al., 1994). The oil shale originated in a lagoon on the sea coast (Vass et al. 1994).

The carbonatic lamina in oil shale from Shushevlyanska Bela Stena, and/or in oil shale of the Valyevo–Mionica Depression are built up by the dolomicrite (rarely by calcite) with the authigenic minerals as searlesite, analcime, trona, shortite and gypsum. The minerals testify the relatively high salinity in paleolake and in interstitial brine (Obradović, Djurdjević-Colson & Vlasič, 1997).

The sample taken from the oil shale outcropping in the town of Mionica near the bridge on the Ribnica river is poor in TOC (1.11 wt.%) and the kerogen is of type III and II. The sampled rock facies originated under different conditions as other sampled Serbian oil shales. When the sampled rock originated, the paleolake was deep enough to enable the summer stagnation in the lake and the sediments originated in the lake are laminated. On the other hand in the epilimnion of the paleolake, and/or its marginal parts the conditions for the nannophytoplankton have not been optimal. The *Botryoccocacea* have been obliged to live together with higher water plants and even with woody plants growing nearby the lake coast. Because of it the kerogen generated from the mixed plant population is of type III and II.

Concerning the oil shales maturation stage the oil shale of Drienovec is less mature as sampled Serbian ones despite the Drienovec oil shale older age. The age of former is Eocene – Oligocene while the age of Serbian oil shales is Lower and Middle Miocene. For instance the age of oil shale in Aleksinac Depression is Lower Miocene (Stevanović, 1964) and the samples of Subotinac (Srb-1 and 2) are in early mature relic stage. The significantly older Drienovec oil shale is in immature stage (Fig. 10). The reason may be the higher heat flow in the Aleksinac Depression. The recent one is about 100 $mW.m^{-2}$ (Milivojević & Martinović, 2000) and the former heat flow was probably higher being elevated by contemporaneous volcanism in the area. The recent heat flow in surroundings of Drienovec is about 70 $mW.m^{-2}$ (Franko et al., eds., 1995) and in the surroundings of Drienovec any manifestation of Cenozoic volcanic activity is missing, so there is no reason to suppose the higher heat flow during the Paleogene.

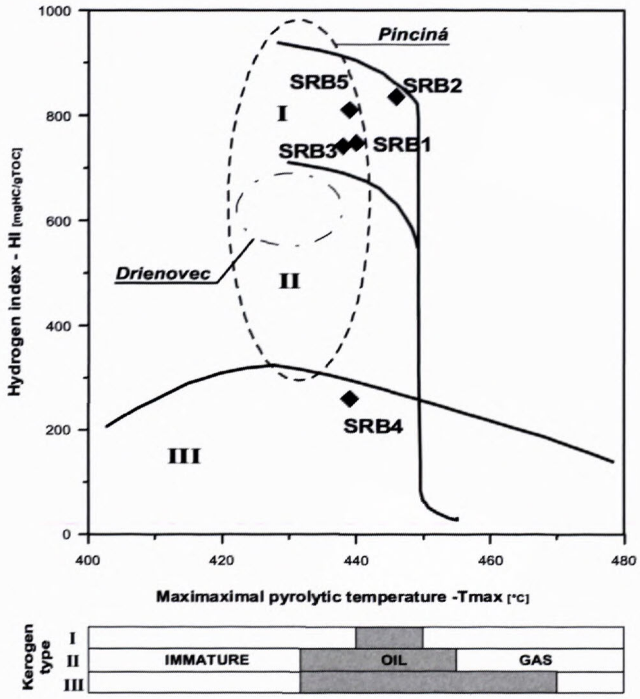

Fig. 10. HI – Tmax diagram showing kerogen type and maturation stage of investigated samples.

Another but less probable reason of the inverse maturity stage of the compared oil shales may be the relatively higher original overburden of the Serbian oil shales under study.

The alginite of Pinciná with prevailing kerogen of type II despite its young age (Pontian) is in early mature relic stage. It is the consequence of coeval elevated paleoheat flow caused by basalt volcanic activity in the Southern Slovakia, lasting from Pontian till the Quaternary.

The relation between total inorganic carbon and total organic carbon contents in the oil shales taken into consideration in this paper and presented in the Fig. 12, indicates the relation ship more TIC contents signify the drop of TOC in oil shales.

The inorganic carbon contents (TIC) of the Aleksinac and Vranye depressions oil shales, as well as of the alginite of Pinciná are low and similar. On the other hand

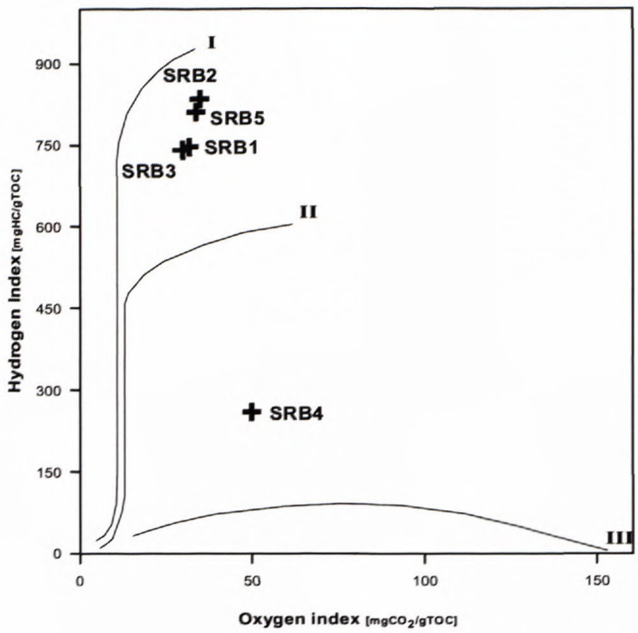

Fig. 11. Kerogen type of Serbian oil shales in OI – HI diagram.

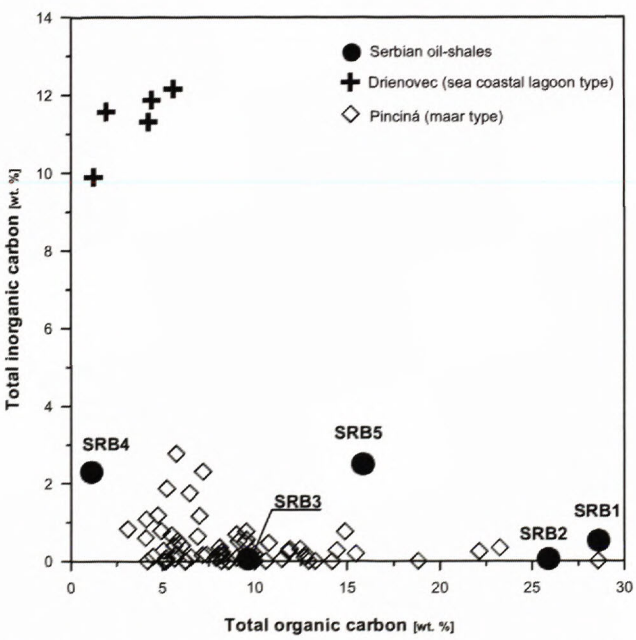

Fig. 12. Comparison of inorganic carbon content in Serbian and Slovak oil-shales.

the TIC contents of the Mionica Depression oil shales (Srb-4 and 5) are higher (by 2 wt.%) and of Drienovec oil shale much more higher (by 10 to 12 wt.%, Fig. 12). The TIC contents reflect conditions of deposition environment and the rock composition in the source area. The oil shales of Aleksinac and Vranye depressions and of Pinciná maar originated in paleolakes supplied by fine clastic material – by clay coming from weathered source rocks. The oil shales of Mionica Depression originated in the paleolake supplied by the carbonates in solution. The salinity of the lake was elevated and dolomicrite layers with the authigenic chemogene minerals after seasonal summer stagnation originated. The Drienovec oil shale originated in the sea costal lagoon, in condition resembling the carbonate shelf platform. After seasonal stagnation when the lagoon was crowded by the Algae rich in oil, the season of calcareous Algae growth followed and thin carpets of those Algae covered the lagoon bottom, giving origin to the white in organic matter poor laminas.

Conclusions

In the Serbian Cenozoic lacustrine deposits beside other sedimentary rock types the oil shales occur. Organic matter of five randomly selected oil shale samples coming from three depressions: Aleksinac, Valyevo–Mionica and Vranye–Polyanica was characterized using elementary analysis and Rock-Eval pyrolysis. Fossil content and paleoecological conditions were characterized and verified by palynological study. According to results of analyses, the samples from Subotinac, Vranye and Shushevlyanska Bela Stena correspond to aquatic kerogen type I, being rich in organic carbon content (10–30 wt.%), as well as in hydrogen content expressed by hydrogen index (HI = 740–840 mg HC/g TOC). Sample from Mionica represents kerogen type III derived from woody material. According to maximal pyrolytic temperature all investigated samples are in the early mature relict stage. The relatively high maturation of oil shale kerogen indicates the elevated paleoheat flow in Central and Southern Serbia.

Oil shales from Aleksinac and Valyevo–Mionica depressions are Miocene in age and they originated under humid subtropical climate. The oil shales from Vranye–Polyanica Depression are Oligocene in age and originated under tropical to subtropical climate conditions. The oil shales originated in relatively large and deep lakes well supplied by nutritive elements and the water was seasonally eutrophic. The laminated structure of oil shales testifies the annual climatic changes. Small size of *Botryococcus* cells particularly of Aleksinac Depression oil shales indicates the excellent live conditions and high reproduction potential of the algae. The same is testified by the high content of TOC and by the dominant kerogen type I.

Rise of TIC contents in oil shales of Valyevo–Mionica Depression reflects the decrees of TOC contents. The inorganic carbon comes from the authigenic chemogene minerals because the salinity of the lakes was elevated. The pristane/phytane ratio in the oil shales of Aleksinac Depression is generally less than 1, indicating an origin in a saline lake rich in dissolved carbonates.

Comparison with the Cainozoic oil shales of Central Europe indicates the differences in paleolake size, in paleoheat flow intensity and in carbonate lamina origin. Particularly the maar lakes of Slovakia and Hungary were small. The paleoheat flow in surroundings of Drienovec (Slovakia) was significantly lower in comparison with that in Central and Southern Serbia. The Drienovec oil shales differ from those of Shushevlyanska Bela Stena in the origin of organic matter free lamina. Those of Drienovec originated by the activity of calcareous algae, those of Shushevlyanska Bela Stena are of chemogene origin.

Fig. 13. Sites of Middle Europe oil shales compared with the sampled Serbian oil shales. 1 – Pinciná, 2 – Drienovec, 3 – Šiatorská Bukovinka, 4 – Pula, 5 – Gérce, 6 – Sokolov Coal Basin.

Acknowledgement.

The paper was supported by the Grant agency VEGA, projects No 1/4047/07, 1/3075/06, 2/6045/26 and 2/6093/26

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